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Process for the Production of High-Strength Calcium Silicate Molded Products

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Inventors: Takao Take  
c/o Onoda Cement Co., Ltd.  
Business Development Office  
1-7, 1-chome Hoshu, Edo-ku, Tokyo-to

Katsuaki Kaneko  
c/o Onoda Cement Co., Ltd.  
Business Development Office  
1-7, 1-chome Hoshu, Edo-ku, Tokyo-to

Shigeo Otozaki  
c/o Onoda Cement Co., Ltd.  
Business Development Office  
1-7, 1-chome Hoshu, Edo-ku, Tokyo-to

Applicant: Onoda Cement Co., Ltd.  
6476 Oaza Onoda  
Onoda-shi, Yamaguchi-ken

Agent: Takehiko Suzue, patent attorney, and two others

## SPECIFICATION

### 1. Title of the Invention

Process for the production of high-strength calcium silicate molded products

### 2. Claims

(1) A process for the production of high-strength calcium silicate molded products wherein a slurry is obtained by adding 0.5-3.0% of sodium silicate or potassium silicate as primary hardener versus the total weight of the silicic acid-type raw material and lime-type raw material in a raw material mixture of at least silicic acid-type raw material, lime-type raw material, primary hardener, and water in which crystalline silica and amorphous silica are used as the silicic acid-type raw material and the relationship between the water/solid weight ratio and the amorphous silica/(crystalline silica + amorphous silica) ratio is within the pentagonal range bounded by points A (1.0, 0.50), B (1.0, 0.15), C (4.0, 0.50), D (4.0, 0.60), and E (2.0, 0.60) shown in attached Figure 1, then packed into a mold, the mold removed after primary hardening by heating, and the product subsequently reacted by heating under increased pressure.

(2) A process for the production of high-strength calcium silicate molded products wherein a slurry is obtained by adding 0.5-3.0% of sodium silicate or potassium silicate as primary hardener versus the total weight of lime-type raw material and silicic acid-type raw material in a raw material mixture composed of lime-type raw material, silicic acid-type raw material, primary hardener, fibers, heat-resistant resin, and water in which the mixture ratio of fibers and heat-resistant resin is 2-10% by weight each, crystalline silica and amorphous silica are used as the silicic acid-type raw material, and the relationship between the water/solid weight ratio and the amorphous silica/(crystalline silica + amorphous silica) weight ratio is within the rectangular range bounded by points F (1.0, 0.25), G (1.0, 0.07), H (4.0, 0.45), and I (4.0, 0.55) shown in attached Figure 2, then packed into a mold, the mold removed after primary hardening by heating, and the product subsequently reacted by heating under increased pressure.

(3) The process for the production of high-strength calcium silicate molded products of Claim 1 or 2 wherein 0.1-1.5% of sodium silicofluoride versus the total weight of the silicic acid-

type raw material and lime-type raw material is added in addition to sodium silicate or potassium silicate as the primary hardener.

### 3. Detailed Explanation of the Invention

(Industrial field of utilization)

The present invention relates to an economical process for the production of high-strength calcium silicate molded products.

(Prior art)

Calcium silicate molded products, obtained by hydrothermal synthesis from a silicic acid-type raw material and lime-type raw material, are widely used as construction materials because of excellent properties such as light weight, high strength, heat resistance, and workability.

Conventional methods of producing calcium silicate molded products are broadly divided into (1) wet squeeze molding, (2) molding by papermaking machine, (3) semidry molding, (4) extrusion molding, and (5) cast molding. However, problems with each of these molding methods have been pointed out in the past.

Specifically, the bulk density of molded products obtained by all methods except cast molding is limited to a certain narrow range. Wet squeeze molding and semidry molding also require large presses and papermaking equipment. Extrusion molding also requires extrusion equipment. All of these requirements greatly increase the equipment cost and result in raising the production cost. Cast molding fills a mold with the raw material slurry, places the mold as is in an autoclave, and molds the slurry by reacting it by heating under increased pressure. Even though this resolves the problem of the narrow bulk density range of the molded products obtained, this method creates a new problem in that it requires heavy molds for production. ←

US Patent No. 2,432,981 concerns a technique for raising the turnover of the mold to resolve the aforementioned drawbacks of cast molding. This technique uses the amorphous silica diatomaceous earth as the silicic acid-type raw material, and adds lime and sodium hydroxide and bentonite as hardeners to it, mixes the resultant mixture with a fiber type raw material and water.

packs it into a mold, removes the mold after primary hardening by heating, then dries the product after reacting it by heating under increased pressure. US Patent No. 2,904,444 discloses another method that uses the amorphous silica diatomaceous earth as the silicic acid-type raw material, adds lime, water-free sodium silicate or water-free potassium silicate as hardener, and granulated sugar as an agent to delay hardening to it, then combines a fiber-type raw material and water to produce a slurry which is packed into a mold, the mold removed after primary hardening by heating, and the product subsequently dried after reacting by heating under increased pressure. Even though these methods do obtain primary hardened products of a hardness that permits handling at the time the mold is removed, the new problem is the marked reduction in the strength of the final product that has been reacted by heating under increased pressure. Therefore, the current situation is that the products obtained here cannot be used as construction materials as they are.

(Problems to be resolved by the invention)

The object of this invention is to obtain high-strength calcium silicate molded products with a hardness of the primary molded product after removal of the mold sufficient to tolerate handling as well as strength of the final molded product obtained by reacting by heating thereafter under increased pressure adequate to serve as a construction material by cast molding calcium silicate molded products.

(Means of problem resolution)

The present invention is a process for the production of high-strength calcium silicate molded products wherein a slurry is obtained by adding 0.5-3.0% of sodium silicate or potassium silicate as primary hardener versus the total weight of the silicic acid-type raw material and lime-type raw material in a raw material mixture of at least silicic acid-type raw material, lime-type raw material, primary hardener, and water in which crystalline silica and amorphous silica are used as the silicic acid-type raw material and the relationship between the water solid weight ratio and the amorphous silica/crystalline silica ratio is within the pentagonal range bounded by points A (1.0, 0.50), B (1.0, 0.15), C (4.0, 0.50), D (4.0, 0.60), and E (2.0, 0.60) shown in attached Figure 1, then packed into a mold, and the mold removed after primary hardening by

heating, and the product subsequently reacted by heating under increased pressure (Claim 1), a process for the production of high-strength calcium silicate molded products wherein a slurry is obtained by adding 0.5-3.0% of sodium silicate or potassium silicate as primary hardener versus the total weight of lime-type raw material and silicic acid-type raw material in a raw material mixture composed of lime-type raw material, silicic acid-type raw material, primary hardener, fibers, heat-resistant resin, and water in which the mixture ratio of fibers and heat-resistant resin is 2-10% by weight each, crystalline silica and amorphous silica are used as the silicic acid-type raw material, and the relationship between the water/solid weight ratio and the amorphous silica/(crystalline silica + amorphous silica) weight ratio is within the rectangular range bounded by points F (1.0, 0.25), G (1.0, 0.07), H (4.0, 0.45), and I (4.0, 0.55) shown in attached Figure 2, then packed into a mold, and the mold removed after primary hardening by heating, and the product subsequently reacted by heating under increased pressure (Claim 2), and the process for the production of high-strength calcium silicate molded products of Claim 1 or 2 wherein 0.1-1.5% of sodium silicofluoride versus the total weight of the silicic acid-type raw material and lime-type raw material is added in addition to sodium silicate or potassium silicate as the primary hardener (Claim 3).

These inventions will be explained in greater detail below, beginning with the invention of Claim 1.

In the invention of Claim 1, the major raw materials of the molded product are the silicic acid-type raw material, lime-type raw material, and primary hardener. It is optional to also use fibers and other reinforcing materials as necessary.

Crystalline silica and amorphous silica combined in the special ratio explained below are used as the silicic acid-type raw material. Quartz is preferred as the crystalline silica. A fine particle size of the quartz is preferable for shortening the reaction time. For example, quartz graded by particle size so that the fraction remaining on a 250 mesh sieve is no more than 10% is good. Diatomaceous earth, zeolite, silica flour, etc., can be used as the amorphous silica. Diatomaceous earth is preferred. Its particle size should be no more than 10  $\mu$ m.

Slaked lime, raw lime, milk of lime obtained by digesting raw lime in water, and mixtures thereof are used as the lime-type raw material. Slaked lime or raw lime is preferred when the

water/solid weight ratio is less than 2.0. Milk of lime is preferred when the water/solid weight ratio is more than 2.0.

The mixture ratio of silicic acid-type raw material and lime-type raw material is preferably 0.7-1.1 for a  $\text{CaO/SiO}_2$  molar ratio. Sodium silicate or potassium silicate is used as the primary hardener. The percentage added is 0.5-3.0%. Less than 0.5% has no effect. More than 3.0% is not desirable because the strength of the final product produced by reaction by heating under increased pressure decreases. Reinforcing materials are used arbitrarily as necessary to improve the strength of the product. Although the type of reinforcing material does not matter particularly, examples include but are not limited to pulp fibers, nylon fibers, polyester fibers, and inorganic fibers such as rock wool and asbestos. The amount of organic fibers used is preferably 0.5-5.0% versus the total weight of silicic acid-type raw material and lime-type raw material to make the product nonflammable as a construction material.

Of particular note among the aforementioned raw materials is the silicic acid-type raw material. It is a combination of crystalline silica and amorphous silica in a special ratio in the present invention. However, the special mixture ratio of crystalline silica and amorphous silica of the present invention varies depending on the water/solid weight ratio in the raw material.

Specifically, the water/solid weight ratio of the raw material is increased to give the raw material that has been hardened by casting in the mold (primary hardened product) enough strength to permit handling. Therefore, the proportion of amorphous silica in the silicic acid-type raw material must be increased. On the other hand, the water/solid weight ratio of the raw material is preferably 1.0-4.0 in the present invention. The raw material mixture does not have good fluidity and is not suitable for cast molding when the ratio is less than 1.0. The amounts of amorphous silica and primary hardener added must be increased greatly when the water/solid weight ratio exceeds 4.0. The strength of the final product decreases and it becomes impossible to obtain the target product in such cases. However, the proportion of amorphous silica must be increased as the water/solid weight ratio rises as described above even when this water/solid weight ratio is within the 1.0-4.0 range.

The present inventors conducted numerous experiments to study the hardness of the molded product after primary hardening and the flexural strength of the final product in terms of the

relationship between the water/solid weight ratio and the ratio of crystalline silica and amorphous silica. These experiments were conducted under the following conditions.

(Experimental conditions)

Water/solid weight ratios were selected between 0.7 and 4.5. Toriyane silica with a fraction remaining on a 250 mesh sieve of less than 0.1% was used as the crystalline silica. Diatomaceous earth of no more than 50  $\mu\text{m}$  was used as the amorphous silica. Slaked lime powder with a fraction remaining on a 250 mesh sieve of no more than 0.1% was used as the lime-type raw material. The raw materials were mixed so that the  $\text{CaO}/\text{SiO}_2$  molar ratio would be 0.8. 1.0% sodium silicate (water glass no. 1) was added as primary hardener. 5% pulp (Canadian standard freeness 350 mL) was added mixed with water as reinforcing material. This raw material mixture was packed into a mold made of epoxy resin that had interior dimensions of 303 mm  $\times$  606 mm  $\times$  12 mm (height) and had been preheated to 100°C. The surface was leveled. This mold was placed in a steam-curing box and 100°C saturated water vapor blown into the box. The primary hardened product was removed from the mold after maintaining a slurry temperature of 90°C for 20 minutes. The hardness of the primary hardened product was measured using a rubber hardness meter (JIS 6301 model A). This primary hardened product was then placed in an autoclave and reacted for 8 hours at 180°C with 10 kg  $\text{cm}^{-2}$  vapor pressure. The pressure was subsequently lowered to atmospheric pressure and the product removed from the autoclave. The final product was produced by drying in a 105°C oven until the adhered water content was no more than 5%.

The results are shown in Tables 1(1) and (2) and in Figure 1. The relative strength was also determined in the belief that the strength of the final product should be judged in relationship to the bulk density. These results are also shown in Tables 1(1) and (2).

Table 1(1).

No.	Water/Sand weight ratio	Diatomaceous earth Silica diatomaceous earth	Hardness of primary hardened product (hardness meter scale)	Properties of final product			Comments
				Bone-dry bulk density $\rho$ (g/cm <sup>3</sup> )	Flexural strength of molded product $\sigma$ (kg/cm <sup>2</sup> )	Relative strength $\sigma/\rho^2$	
1	0.5	0.20	43	0.72	63.2	122	Inadequate strength
2	0.5	0.40	59	0.71	58.0	115	Inadequate strength
3	1	0.05	12	-	-	-	Inadequate primary hardness
4	1.0	0.10	27	0.67	66.9	149	Inadequate primary hardness
5	1.0	0.15	34	0.67	66.0	147	Inadequate primary hardness
6	1.0	0.20	40	0.68	67.0	145	Inadequate primary hardness
7	1.0	0.30	52	0.67	61.5	137	Inadequate primary hardness
8	1.0	0.40	57	0.68	61.0	132	Inadequate primary hardness
9	1.0	0.50	63	0.67	56.1	125	Inadequate primary hardness
10	1.0	0.55	65	0.68	55.5	120	Inadequate primary hardness
11	1.0	0.70	70	0.68	48.1	104	Inadequate primary hardness
12	1.5	0.17	28	0.54	48.1	165	Inadequate strength
13	1.5	0.21	33	0.54	47.2	162	Inadequate strength
14	1.5	0.29	44	0.55	46.3	153	Inadequate primary hardness
15	1.5	0.38	52	0.55	43.9	145	Inadequate primary hardness
16	1.5	0.47	57	0.54	39.1	134	Inadequate primary hardness
17	1.5	0.55	62	0.55	38.1	126	Inadequate primary hardness
18	1.5	0.60	64	0.54	34.7	119	Inadequate primary hardness
19	2.0	0.10	13	-	-	-	Inadequate strength
20	2.0	0.23	28	0.44	35.2	182	Inadequate strength
21	2.0	0.28	34	0.43	32.5	176	Inadequate strength



22	2.0	0.33	41	0.44	32.7	169	Inadequate primary hardness
23	2.0	0.40	47	0.44	31.0	160	Inadequate primary hardness
24	2.0	0.51	56	0.43	26.1	141	Inadequate primary hardness
25	2.0	0.60	62	0.43	23.5	127	Inadequate primary hardness
26	2.0	0.63	63	0.44	23.2	120	Inadequate primary hardness
27	2.0	0.80	69	0.43	19.6	106	Inadequate primary hardness
							Inadequate strength Inadequate strength

Table 1(2).

No	Water/Sand weight ratio	Diatomaceous earth Silica + diatomaceous earth	Hardness of primary hardened product (hardness meter scale)	Properties of final product			Comments
				Bone-dry bulk density $\rho$ ( $\text{g}/\text{cm}^3$ )	Flexural strength of molded product $\sigma$ ( $\text{kg}/\text{cm}^2$ )	Relative strength $\sigma/\rho$	
28	2.5	0.28	27	0.35	20.5	167	Inadequate primary hardness
29	2.5	0.34	35	0.35	19.6	160	
30	2.5	0.43	49	0.36	19.2	148	
31	2.5	0.53	52	0.36	17.6	136	
32	2.5	0.60	57	0.35	15.6	127	
33	2.5	0.63	59	0.36	15.6	120	
34	3.0	0.20	10	-	-	-	Inadequate strength
35	3.0	0.30	23	0.30	14.1	157	Inadequate primary hardness
36	3.0	0.35	28	0.30	13.7	152	
37	3.0	0.40	32	0.30	13.1	146	Inadequate primary hardness
38	3.0	0.46	39	0.31	13.5	140	
39	3.0	0.55	48	0.31	12.6	131	Inadequate primary hardness
40	3.0	0.60	53	0.30	11.3	126	
41	3.0	0.63	55	0.31	11.3	118	
42	3.0	0.80	62	0.30	8.8	98	
43	3.5	0.41	28	0.25	8.8	141	
44	3.5	0.45	33	0.25	8.6	138	
45	3.5	0.53	40	0.26	8.9	132	Inadequate strength
46	3.5	0.60	45	0.25	7.9	126	Inadequate strength
47	3.5	0.63	47	0.25	7.6	122	Inadequate primary hardness
48	4.0	0.30	9	-	-	-	
49	4.0	0.40	22	0.22	6.6	136	
50	4.0	0.46	28	0.23	7.0	132	

51	4.0	0.50	32	0.22	6.3	130	Inadequate strength
52	4.0	0.60	40	0.22	6.1	126	Inadequate primary
53	4.0	0.63	42	0.23	6.5	123	hardness
54	4.0	0.70	47	0.22	5.3	110	Inadequate primary
55	4.5	0.52	23	0.19	5.0	139	hardness
56	4.5	0.58	28	0.19	4.3	119	Inadequate primary
							hardness
							Inadequate strength
							Inadequate strength
							Inadequate primary
							hardness
							Inadequate primary
							hardness and strength

(Note) The notation "inadequate primary hardness" in the Comments column means a hardness of the primary hardened product of less than 30 by hardness meter scale. "Inadequate strength" means a relative strength of less than 125.

The relative strength of the samples supplied for experimentation shown in Tables (1) and (2) must be at least 125 to come under consideration as a construction material. Assuming 125 to be the lower limit of relative strength in this way, the relationship between the water/solid weight ratio and amorphous silica versus the total of crystalline silica and amorphous silica must fall within the pentagonal range bounded by points A (1.0, 0.50), B (1.0, 0.15), C (4.0, 0.50), D (4.0, 0.60), and E (2.0, 0.60) shown in Figure 1.

As described above, a slurry produced by kneading the raw material with water is poured into a mold and hardened within the mold by the action of the amorphous silica and primary hardener by heating. Heating can be carried out at 70-100°C. However, 20-30 minutes at 90-100°C is preferred from the standpoint of productivity. The product can be removed from the mold without any problem because a primary hardened product that maintains self support and good handleability is obtained in this way. The measure of the degree of hardening in this case is that the hardened product develops no cracks, broken corners, or dimples when handled. A simple measurement method is measurement of the hardness of the hardened product by rubber hardness meter (JIS 6301 model A). The display scale should be at least 30.

After the primary hardened product is removed from the mold, it is placed in an autoclave and heated under increased pressure. The reaction conditions are preferably 2-12 hours at a pressure of at least  $10 \text{ kg cm}^{-2}$  and a temperature of at least 180°C. The final product is obtained by removing it from the autoclave and drying after the reaction has been completed. The bone-dry bulk density of the product ranges from 0.2 to 0.7. Potassium silicate can also be used as a primary hardener, as is understood from practical examples 4 and 5 below.

Next, the invention of Claim 2 will be explained. The major raw materials of this invention are the same as those of the invention of Claim 1, i.e., silicic acid-type raw material, lime-type raw material, and primary hardener. Those explained for the invention of Claim 1 can be used as the silicic acid-type raw material and lime-type raw material.

Specifically, crystalline silica and amorphous silica are used as the silicic acid-type raw material. These are used after adjusting them to the necessary particle size. The mixture ratio of crystalline silica and amorphous silica in the silicic acid-type raw material varies in relationship to the water/solid weight ratio in the raw material, in the same way as in the invention of Claim 1. However, the relationship here differs slightly from that of the invention of Claim 1, as will be

discussed below. The lime-type raw material is also the same as the invention of Claim 1. The primary hardener is also the same as in the invention of Claim 1. Sodium silicate or potassium silicate is used.

Fibers and heat-resistant resin are used as secondary raw materials in addition to the major raw materials in this invention.

Fibers include inorganic fibers such as glass fibers, asbestos, rock wool, acicular wohlastonite, and fibrous sepiolite, pulp fibers, carbon fibers, nylon fibers, vinylon fibers, and polyester fibers. Glass fibers are especially effective for improving performance. Therefore, it is preferable to use glass fibers as part of the fibers used. The amount of fibers used is preferably 2-10% by weight by mixture ratio in the total raw material. The desired effects on the strength and toughness of the product obtained are not obtained when the amount used is less than 2% by weight. The effects do not improve further when the amount exceeds 10% by weight.

Heat-resistant resins include acrylic resins, styrene resins, melamine resins, ethylene-vinyl acetate resins, phenol resins, and copolymer resins thereof. These resins are preferably used in the form of an aqueous emulsion to allow them to mix homogeneously with the other raw materials. An aqueous emulsion of acrylic resin or acrylic-styrene copolymer resin is preferred. The mixture ratio of heat-resistant resin is appropriately 2-10% by weight, calculated based on the solids fraction.

The desired effects on the strength and toughness of the product obtained are not obtained when the amount added is less than 2% by weight. There is no further improvement of the effects above 10% by weight. The mixture ratio of amorphous silica necessary to accelerate primary hardening during molding can be decreased when the aforementioned fibers and resins are used.

As was already mentioned, the mixture ratio of crystalline silica and amorphous silica in the silicic acid-type raw material varies in relationship to the water/solid weight ratio in the raw material in the invention of Claim 2, in the same way as in the invention of Claim 1. However, the relationship between the mixture ratio of crystalline silica and amorphous silica in the silicic acid-type raw material and the water/solid weight ratio in the raw material differs from that of the invention of Claim 1 because fibers and heat-resistant resins are combined with the raw material.

The inventors conducted numerous studies of this point, in the same way as for the invention of Claim 1, and studied the hardness of the molded product after primary hardening and the flexural strength, etc. of the final product in terms of the relationship between the ratio of crystalline silica

and amorphous silica and the water/solid weight ratio. The experimental conditions of these studies were as follows.

(Experimental conditions)

Water/solid weight ratios of 1.0-4.0 were selected. Toriyane silica with a fraction remaining on a 250 mesh sieve of less than 0.1% was used as a crystalline silica. Diatomaceous earth of no more than 50  $\mu\text{m}$  was used as the amorphous silica. Slaked lime powder with a fraction of less than 0.1% remaining on a 250 mesh sieve was used as the lime-type raw material, combined so that the  $\text{CaO}/\text{SiO}_2$  molar ratio would be 0.85. 1.0% of sodium silicate (water glass no. 1) or potassium silicate, calculated based on the solids fraction, was added as primary hardener. 3.0% alkali-resistant glass fibers (diameter 13  $\mu\text{m}$ , length 13 mm) as reinforcing material and 3.0% acrylic-styrene copolymer resin emulsion (solids fraction 54.2%, pH 9.0, anionic), calculated based on the solids fraction, as heat-resistant resin were also added together with water. This raw material mixture was packed into a mold made of epoxy resin with inner dimensions of 303 mm  $\times$  606 mm  $\times$  12 mm (height) that had been preheated to 100°C, and the surface leveled. This mold was placed in a steam-curing box and 100°C saturated water vapor introduced. The product was removed from the mold as the primary hardened product after maintaining a slurry temperature of 90°C for 20 minutes. The hardness of the primary hardened product was measured by rubber hardness meter (JIS 6301 model A). This primary hardened product was placed in an autoclave and reacted for 4 hours at 10 kg/cm<sup>2</sup>, 180°C. After subsequently lowering the pressure to atmospheric pressure and removing the product from the autoclave, the final product was obtained by drying in a 105°C oven until the adhered water fraction became no more than 1%. These results are shown in Table 2 and Figure 2. The relative strength of the final product was also determined and is shown in Table 2 and Figure 2. The fluidity of the raw material slurry was very poor in numbers 7, 11, 17, 22, and 27. The inability to pour the slurry into the mold to form it made measurement of the properties impossible.

Table 2.

No.	Water/Solid weight ratio	Diatomaceous earth Silica + diatomaceous earth	Hardness of primary hardened product (hardness meter scale)	Properties of final product			Comments
				Bone-dry bulk density $\rho$ (g/cm <sup>3</sup> )	Flexural strength of molded product $\sigma$ (kg/cm <sup>2</sup> )	Relative strength $\sigma/\rho$	
1	1.0	0.05	22	0.68	101.3	219	Inadequate primary hardness
2	1.0	0.07	32	0.67	97.0	216	
3	1.0	0.10	37	0.67	90.2	201	
4	1.0	0.15	41	0.68	90.6	196	
5	1.0	0.20	46	0.67	79.9	178	
6	1.0	0.25	48	0.68	76.3	165	
7	1.0	0.30	-	-	-	-	Cast molding impossible
8	1.0	0.17	35	0.55	73.5	243	
9	1.0	0.21	41	0.54	65.6	225	
10	1.0	0.29	53	0.55	55.1	182	
11	1.0	0.38	-	-	-	-	Cast molding impossible
12	1.0	0.17	31	0.54	68.8	236	
13	1.0	0.21	37	0.55	65.6	217	
14	2.0	0.10	20	0.43	40.1	217	Inadequate primary hardness
15	2.0	0.23	36	0.43	36.6	198	
16	2.0	0.28	40	0.43	33.3	180	
17	2.0	0.37	-	-	-	-	Cast molding impossible
18	3.0	0.20	18	-	-	-	Cast molding impossible
19	3.0	0.30	27	0.31	22.2	231	Inadequate primary hardness
20	3.0	0.35	34	0.30	18.0	200	
21	3.0	0.40	38	0.31	16.9	176	Inadequate primary hardness
22	3.0	0.46	-	-	-	-	
23	4.0	0.40	28	0.22	11.4	228	

24	4.0	0.46	35	0.22	10.6	219	Cast molding impossible Inadequate primary hardness
25	4.0	0.50	37	0.22	9.2	191	
26	4.0	0.55	40	0.22	8.2	169	
27	4.0	0.60	-	-	-	-	
							Cast molding impossible

(Note 1: The notation "inadequate primary hardness" in the Comments column means the same as in Table 1.

(Note 2: Potassium silicate was used as the primary hardener in numbers 12 and 13. Sodium silicate was used in the other examples.



When the weight ratio of amorphous silica/(crystalline silica + amorphous silica) was higher than line F-I in Figure 2, the fluidity of the raw material slurry decreased and made cast molding difficult. The inadequate primary hardness of the hardened product made handling difficult below line G-H in the same figure.

Therefore, as shown in Figure 2, the relationship between the water/solid weight ratio and the amorphous silica/(crystalline silica + amorphous silica) weight ratio must be within the rectangular range bounded by points F (0.1, 0.25), G (1.0, 0.07), H (4.0, 0.45), and I (4.0, 0.55) in Figure 2 because fibers and heat-resistant resins are combined with the raw material in the invention of Claim 2.

As described above, the specified raw materials are kneaded with water to make a slurry, poured into a mold, hardened by heating, and a primary hardened product obtained by removal from the mold. This is the same as in the invention of Claim 1. Next, this primary hardened product is placed in an autoclave and reacted by heating under increased pressure. The product is obtained by drying after removal from the autoclave after the reaction has been completed. This is also the same as the invention of Claim 1.

0.1-1.5% sodium silicofluoride is added versus the total weight of silicic acid-type raw material and lime-type raw material in addition to sodium silicate or potassium silicate as primary hardener in the invention of Claim 3. This can further raise the strength of the final product.

#### (Effects of the invention)

The present invention explained above can obtain a primary hardened product with adequate strength for handling as well as a high-strength calcium silicate molded products with high final product strength merely by varying the mixture ratio of crystalline silica and amorphous silica in the silicic acid-type raw material, which is one of the raw materials used, in relationship to the water/solid weight ratio. Furthermore, the present invention permits the bone-dry bulk density of the final product to range widely from approximately 0.2 to 0.7. This allows one to make various construction materials such as heat-insulating materials, divider materials, wall materials, and ceiling materials using the same equipment.

### Practical examples 1-3

Toriyane silica powder with a 0.1% fraction remaining on a 250 mesh sieve as crystalline silica and diatomaceous earth of no more than 50  $\mu\text{m}$  as amorphous silica were used as the silicic acid-type raw material. These were used mixed in the mixture ratios show in Table 2. This silicic acid-type raw material and slaked lime powder with a fraction of no more than 0.1% remaining on a 250 mesh sieve were mixed to make a  $\text{CaO}/\text{SiO}_2$  molar ratio of 0.9. 2.0% sodium silicate (water glass no. 1) was added as primary hardener. 3% alkali-resistant glass fibers with a diameter of 9  $\mu\text{m}$  and length of 13 mm were added as reinforcing material, mixed with water. This raw material mixture was packed into a mold made of epoxy resin with inner dimensions of 910 mm  $\times$  1820 mm preheated to 100°C, and the surface leveled. This mold was placed in a steam-curing box and 100°C saturated water vapor introduced. The primary hardened product was removed from the mold after maintaining for 20 minutes at a slurry temperature of 90°C. This primary hardened product was placed in an autoclave and reacted for 10 hours at 10 kg/cm<sup>2</sup>, 180°C. The pressure was subsequently lowered to atmospheric pressure and the product removed from the autoclave and dried in a 105°C oven until the adhered water fraction was no more than 5% to obtain the final product. Table 3 shows the hardness of the primary hardened product and the properties of the final product.

Table 3.

	Water/Solid weight ratio	Diatomaceous earth — Silica · diatomaceous earth	Hardness of primary hardened product (hardness meter scale)	Properties of final product		
				Bone-dry bulk density $\rho$ (g/cm <sup>3</sup> )	Flexural strength of molded product (kg/cm <sup>2</sup> )	Relative strength $\sigma/\rho^2$
Practical example						
1	1.0	0.35	50	0.67	72.2	163
2	2.0	0.35	46	0.44	36.2	187
3	3.0	0.40	37	0.31	16.0	166

Practical examples 4 and 5

The same studies were conducted as in practical examples 1 and 3 except that 2.0% potassium silicate was added as primary hardener. The results are shown in Table 4.

Table 4.

	Water/Sol id weight ratio	Diatomaceou s earth  — Silica + diatomaceou s earth	Hardness of primary hardened product (hardness meter scale)	Properties of final product		
				Bone-dry bulk density $\rho$ (g/cm <sup>3</sup> )	Flexural strength of molded product (kg/cm <sup>2</sup> )	Relativ e strengt h $\sigma/\rho^2$
Practical example						
4	1.0	0.25	48	0.68	73.1	158
5	3.0	0.40	34	0.30	15.0	167

Practical examples 6-8

The studies were the same as in practical examples 1-3 except that 2.6% sodium silicate (water glass no. 1) and 0.4% sodium silicofluoride were added as primary hardener. The results are shown in Table 5.

Table 5.

	Water/Sol id weight ratio	Diatomaceou s earth  — Silica + diatomaceou s earth	Hardness of primary hardened product (hardness meter scale)	Properties of final product		
				Bone-dry bulk density $\rho$ (g/cm <sup>3</sup> )	Flexural strength of molded product (kg/cm <sup>2</sup> )	Relativ e strengt h $\sigma/\rho^2$
Practical example						
6	1.0	0.25	53	0.68	85.5	185

7	2.0	0.35	49	0.43	37.0	200
8	3.0	0.40	40	0.31	18.3	190

The strength of the final product increased when sodium silicofluoride was added in addition to the sodium silicate as primary hardener in comparison to when sodium silicate was used alone. Practical examples 9-11

Toriyane silica powder with a 0.1% fraction remaining on a 250 mesh sieve as crystalline silica and diatomaceous earth of no more than 50  $\mu\text{m}$  as amorphous silica were used as the silicic acid-type raw material. These were used mixed in the mixture ratios show in Table 6. This silicic acid-type raw material and slaked lime powder with a fraction of no more than 0.1% remaining on a 250 mesh sieve were mixed to make a  $\text{CaO}/\text{SiO}_2$  molar ratio of 0.85. 5.0% alkali-resistant glass fibers (diameter 13  $\mu\text{m}$ , length 13 mm) as reinforcing material and 5.0% (calculated based on the solids fraction) acrylic-styrene copolymer resin emulsion (solids fraction 54.2%, pH 9.0, anionic) as heat-resistant resin were also added. 2% sodium silicate (water glass no. 1) was added as primary hardener, mixed with water. This raw material mixture was packed into a mold made of epoxy resin with inner dimensions of 303 mm  $\times$  606 mm  $\times$  15 mm (height) preheated to 100°C, and the surface leveled. This mold was placed in a steam-curing box and 100°C saturated water vapor introduced. The primary hardened product was removed from the mold after maintaining for 20 minutes at a slurry temperature of 90°C. This primary hardened product was placed in an autoclave and reacted for 4 hours at 10 kg/cm<sup>2</sup>, 180°C. The pressure was subsequently lowered to atmospheric pressure and the product removed from the autoclave. The final product was obtained by drying in a 105°C oven until the adhered water fraction was no more than 1%. The results are shown in Table 6.

Table 6.

	Water Sol id weight ratio	Diatomaceo- s earth - Silica - diatomaceou s earth	Hardness of primary hardened product (hardness meter scale)	Properties of final product		
				Bone-dry bulk density $\rho$ (g/cm <sup>3</sup> )	Flexural strength of molded product (kg/cm <sup>2</sup> )	Relativ e strengt h $\sigma/\rho^2$

Practical example						
9	1.0	0.10	38	0.68	126.7	274
10	2.0	0.23	38	0.43	50.1	271
11	3.0	0.35	37	0.31	26.5	276

#### Practical examples 12-14

The studies were the same as practical examples 9-11 except that 2.6% sodium silicate (water glass no. 1) and 0.4% sodium silicofluoride were added as primary hardener. The results are shown in Table 7.

Table 7.

	Water/Solid weight ratio	Diatomaceous earth — Silica + diatomaceous earth	Hardness of primary hardened product (hardness meter scale)	Properties of final product		
				Bone-dry bulk density $\rho$ (g/cm <sup>3</sup> )	Flexural strength of molded product (kg/cm <sup>2</sup> )	Relative strength $\sigma/\rho^2$
Practical example						
12	1.0	0.10	42	0.68	138.7	300
13	2.0	0.23	43	0.43	54.9	297
14	3.0	0.35	42	0.31	29.0	302

#### 4. Brief Explanation of the Figures

Figures 1 and 2 are line diagrams that show the relationship between the water solid weight ratio and the weight ratio of amorphous silica/(crystalline silica + amorphous silica) in the raw material used to produce calcium silicate.

Figure 1.

Key: a) Amorphous silica/(Crystalline silica + amorphous silica) weight ratio  
B) Water/Solid weight ratio

Figure 2.

Key: a) Amorphous silica/(Crystalline silica + amorphous silica) weight ratio  
b) Water Solid weight ratio